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## DEVELOPMENT OF GREEN LIGHT FILTERS BASED ON HIGH-RESISTANCE OXIDE GLASSES COLORED BY TRANSITION ELEMENTS

L. D. Bogomolova,<sup>1</sup> V. A. Zhachkin,<sup>2</sup> and T. K. Pavlushkina<sup>3</sup>

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Glasses in the system  $\text{Al}_2\text{O}_3\text{--P}_2\text{O}_5\text{--SiO}_2$ , which are suitable for the green light filters in traffic signal lights, were investigated. The glasses were required to satisfy the following requirements: transmission band maximum at  $\lambda_{\text{max}} = 500 \text{ nm}$  high heat-resistance, and low CLTE —  $(41 - 49) \times 10^{-7} \text{ K}^{-1}$ . Transition elements served as colorants; they were introduced into the batch as the oxides  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{CuO}$ , and  $\text{MoO}_3$  in amounts 1 wt.%, as well as their pairs in different combinations. The EPR and optical spectra were investigated. It was shown that glass with the composition (wt.%) 55  $\text{P}_2\text{O}_5$ , 17.1  $\text{Al}_2\text{O}_3$ , 20  $\text{SiO}_2$ , 1.5  $\text{La}_2\text{O}_3$ , 2  $\text{ZrO}_2$ , 2.5  $\text{B}_2\text{O}_3$ , 1.5  $\text{MoO}_3$ , and 0.5  $\text{CuO}$  can be recommended for use as heat-resistant green light filters.

**Key words:** green light filters, signal lights, EPR, optical spectra, transition elements.

Colored light filters are used for signal lights in aviation, railroad, and sea transport. The glasses used for light filters must possess definite characteristics (color, thermal, mechanical, and others) for reliable recognition of the signal color at a considerable distance under different operating conditions (elevated temperature, velocity of the object, atmospheric precipitation, and others).

Glasses which can be used to manufacture green signal light filters were studied in the present work. Glasses to be used for such applications have been developed and used in different organizations, including with the participation of the present authors (for example, [1, 2]). Such glass must be practicable, have a low linear thermal expansion coefficient (CLTE) in the range  $(35 - 50) \times 10^{-7} \text{ K}^{-1}$ , high heat-resistance (no lower than  $300^\circ\text{C}$ ) and light transmission at least 20% near maximum transmission at 500 nm (bluish-green color).

The glasses are usually colored by transition elements (TE). Theoretically and experimentally, the electronic absorption spectra of TE due to transitions between sublevels of the  $d$ -shells ( $d-d$  transitions), which are characterized by small extinction coefficients, lie in the visible, near-UV, and IR frequencies of electromagnetic radiation. The transitions are forbidden by selection rules with respect to the orbital quantum number. In the absence of a center of symmetry (oc-

tahedral environment of the TE) the  $d$  shells can mix with the  $p$  shell as a result of thermal vibrations, making the transitions allowed though weak. In tetrahedral coordination, when a center of symmetry exists, the absorption bands become stronger.

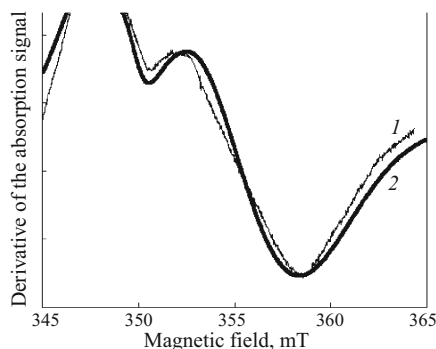
The valence and coordination state of TE and the position and shift of the electronic absorption bands depend on the optical basicity of the glass, which essentially characterizes the capability of oxygen to impart negative charge to a transition element. The basicity of the glasses depends on their properties and is highest in alkali-containing glass. For example, the optical basicity  $\Lambda$ , which can be calculated using the relations presented in [3], equals 0.65 in glass with molar content 40  $\text{Na}_2\text{O}$  and 60  $\text{SiO}_2$ ,  $\Lambda = 0.46$  with 30  $\text{Al}_2\text{O}_3$  and 70  $\text{P}_2\text{O}_5$ , and  $\Lambda = 0.43$  with 33  $\text{SiO}_2$  and 67  $\text{P}_2\text{O}_5$ .

In the present work we studied the optical spectra of some TE in the system  $\text{Al}_2\text{O}_3\text{--P}_2\text{O}_5\text{--SiO}_2$ , for which  $\Lambda$  varies from 0.43 to 0.46 depending on the composition. For these glasses the CLTE varies in the range  $(41 - 49) \times 10^{-7} \text{ K}^{-1}$ ,  $t_g = 683 - 738^\circ\text{C}$ , i.e., the thermal properties satisfy the requirements imposed on the glasses being developed. Oxides of TE were introduced into these glasses in order to obtain the required optical properties. Together with optical measurements, electron paramagnetic resonance (EPR) measurements were also performed; the latter yield information on the valence and coordination states of the coloring ions and their position in the structure of the glasses. Phosphorus-oxygen and silicon-oxygen components coexist in  $\text{Al}_2\text{O}_3\text{--P}_2\text{O}_5\text{--SiO}_2$  glasses and P–O–Si bonds are possible between them.

<sup>1</sup> Scientific–Research Institute of Nuclear Physics, Moscow State University, Moscow, Russia.

<sup>2</sup> Moscow State Regional University, Moscow, Russia.

<sup>3</sup> Glass Institute, JSC, Moscow, Russia (e-mail: tpglass@mail.ru).



**Fig. 1.** EPR spectrum of  $\text{Ti}^{3+}$  in P-50-Ti glass: 1) experimental; 2) computed.

The aluminum cation is predominately located in the phosphate component, while at high  $\text{Al}_2\text{O}_3$  concentration  $\text{AlPO}_4$  structural elements form and can easily combine with  $\text{SiO}_2$ .

## EXPERIMENTAL SAMPLES AND PROCEDURE

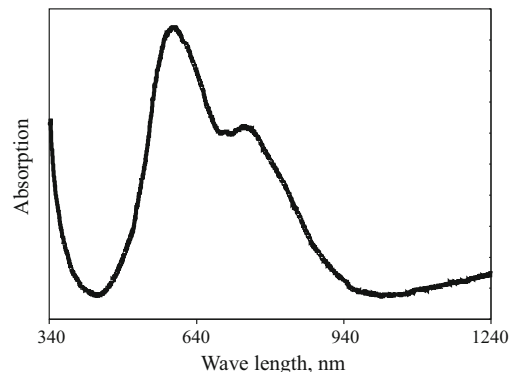
Glasses with two compositions in the system  $\text{Al}_2\text{O}_3$ – $\text{P}_2\text{O}_5$ – $\text{SiO}_2$  were studied as model glass (molar content, %): 50  $\text{P}_2\text{O}_5$ , 30  $\text{Al}_2\text{O}_3$ , 20  $\text{SiO}_2$  (P-50) and 70  $\text{P}_2\text{O}_5$ , 10  $\text{Al}_2\text{O}_3$ , and 20  $\text{SiO}_2$  (P-70). The glasses were synthesized at the Glass Institute, JSC, from chemical-grade reagents (KhCh classification): ammonium monophosphate, aluminum oxide, and anhydrous silicon oxide. Melting was conducted in quartz crucibles in a gas-flame crucible furnace heated by natural gas. The glass-melting temperature 1550–1570°C was held for 1–3 h depending on the composition. The molten glass was poured into a mold placed on a heated metal plate. Depending on the composition the annealing temperature was 550–580°C for 2 h after which the glass was allowed to cool together with the furnace. Some glasses were quenched. The coloring TE were introduced into the batch in the form of the oxides  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{CuO}$ , and  $\text{MoO}_3$  in the amount 1%.<sup>4</sup>

The optical spectra were measured in a SF-8 spectrophotometer at room temperature and wavelengths from 300 to 1200 nm. The EPR spectra were recorded with a modified RE-1306 radio spectrometer with cavity working frequency 9.94 GHz at room temperature. The EPR parameters of the spectra were determined by comparing the experimental and model spectra calculated using the program developed in [4].

The EPR and optical spectra were studied as function of the glass composition, TE concentration, synthesis conditions, and different oxidizing-reducing (OR) additives.

## RESULTS AND DISCUSSION

**Titanium.** Titanium exists in two stable modifications in oxide glasses:  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$ . The  $\text{Ti}^{4+}$  ion is diamagnetic, and only the  $\text{Ti}^{3+}$  ion gives an EPR signal. The EPR signal in



**Fig. 2.** Optical absorption spectrum of P-50-Ti glass.

glass with 1%  $\text{TiO}_2$  (P-50-Ti) is displayed in Fig. 1. The parameters of the spectrum are:  $g_{\parallel} = 1.92$ ;  $g_{\perp} = 1.98$ . Such spectra have been observed in many oxide glasses and are usually ascribed to the  $\text{Ti}^{3+}$  ion in an environment of oxygen ions, forming an octahedron compressed along the tetragonal axis (symmetry group  $C_{4v}$ ). The ground state of this ion is  $^2D$  with five-fold orbital degeneracy. The  $^2D$  state of the  $3d^1$  ions in an octahedral electric field splits into a triplet ground state  $^2T_2$  ( $|xy\rangle$ ,  $|yz\rangle$ ,  $|zx\rangle$ ) and a doublet excited state  $^2E$  ( $|z^2 - 3r^2\rangle$ ,  $|x^2 - y^2\rangle$ ). In a tetragonally distorted field the  $^2T_2$  state splits into a singlet  $|xy\rangle$  and a doublet  $|yz\rangle$ ,  $|zx\rangle$ . Depending on whether the octahedron is stretched or compressed, the ground state will be a doublet ( $^2E$ ) or singlet  $|xy\rangle$ . On the basis of the values of the  $g$  factors it can be concluded that the ground state of  $\text{Ti}^{3+}$  is a singlet  $|xy\rangle$ , while the ion itself is located in a tetragonally compressed octahedron.

Figure 2 shows the optical absorption spectrum for P-50-Ti glass. The spectrum contains an absorption band at 590 nm and a shoulder at 740–750 nm. In octahedral coordination  $\text{Ti}^{3+}$  should give a single absorption band due to the transition  $^2T_{2g} \rightarrow ^2E_{2g}$ . The shoulder could be due to tetragonal distortion of the ligand octahedron. It should be noted that the transmission band in this glass lies at 420 nm and lies in the blue part of the spectrum, i.e., it is shifted into the short wavelength region relative to the prescribed region.

**Vanadium** is usually present in three principal valence states in glasses:  $\text{V}^{3+}$ ,  $\text{V}^{4+}$ , and  $\text{V}^{5+}$ . Pentavalent vanadium gives an electronic absorption band with charge transfer in the near-UV region. Since it is diamagnetic, no EPR signal is observed for it. The two other forms have an absorption band in the near-UV, IR, and visible parts of the spectrum of electromagnetic radiation. Figure 3 displays optical spectra of P-70 and P-50 glasses with 1%  $\text{V}_2\text{O}_5$  (P-70-V and P-50-V). As follows from the figure, for the P-70-V glass (spectrum 1) absorption bands belonging to the  $\text{V}^{3+}$  ion are observed at 370, 450, and 720 nm [5]. In the spectrum of the P-50-V sample (spectrum 2) absorption bands are visible at 380, 680, and 960 nm. The latter two belong to the  $\text{V}^{4+}$  ion [5]. In the P-70 glass the absorption band at 680 nm is apparently covered by a wide and strong band peaking at 720 nm.

<sup>4</sup> Here and below the content by weight.

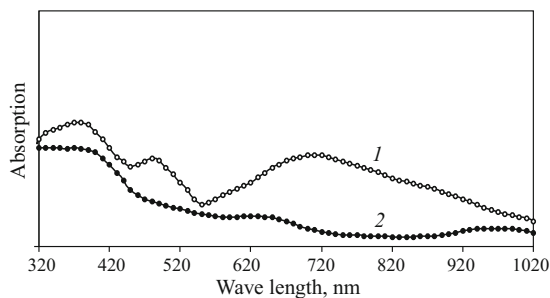


Fig. 3. Optical absorption spectra of P-70-V (1) and P-50-V (2).

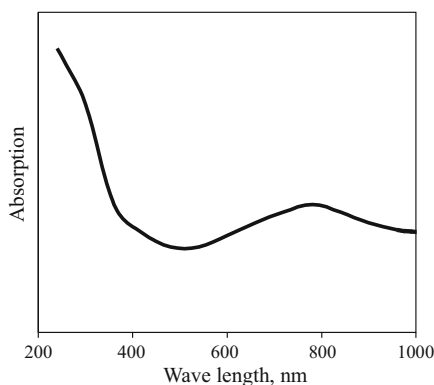


Fig. 4. Optical absorption spectrum of P-50-Cu glass.

Thus, the optical spectra of both samples show the presence of both ions  $V^{3+}$  and  $V^{4+}$ . The transmission band lies at 530 – 550 nm, i.e., it is shifted into the long wavelength part relative to the requirements.

Both samples exhibit EPR spectra. These spectra have a complicated shape due to anisotropic hyperfine structure (HFS), which results from the interaction of an unpaired  $d$  electron of vanadium with the magnetic moment of the  $^{51}V$  nucleus. The nuclear spin of  $^{51}V$  is  $I = 7/2$ . The EPR parameters of the spectrum ( $g_{\parallel} = 1.916$ ,  $g_{\perp} = 1.985$ ,  $A_{\parallel} = 180 \times 10^{-4} \text{ cm}^{-1}$ , and  $A_{\perp} = 74 \times 10^{-4} \text{ cm}^{-1}$ ) calculated using the program of [4] correlate well with data from other works for the systems  $P_2O_5-Al_2O_3-SiO_2$ ,  $P_2O_5-SiO_2$ , and  $P_2O_5-Al_2O_3$  [5]. The  $V^{4+}$  ion has the same electron configuration of the outer electronic shell ( $3d^1$ ) as the  $Ti^{3+}$  ion, and for it the same splitting of the energy levels is valid. The values of the parameters of the spin Hamiltonian indicate that the  $V^{4+}$  ions are in a tetragonally compressed oxygen octahedron (symmetry group  $C_{4v}$ ). It is assumed that V has a short double bond with oxygen, forming the vanadyl ion  $VO^{2+}$ .

Copper is usually present in the two valence states  $Cu^{1+}$  and  $Cu^{2+}$  in glass. The first one is diamagnetic, does not give an EPR signal, and does not have absorption bands in the visible, near-UV, or IR regions of the spectrum. The presence of an optical absorption spectrum (in the visible region) and an EPR spectrum is characteristic for the  $Cu^{2+}$  ion.

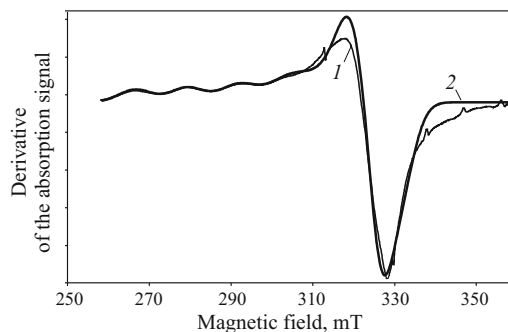


Fig. 5. EPR spectrum of  $Cu^{2+}$  in the glass P-50-Cu: 1) experimental (narrow peaks from the reference sample are observed); 2) computed spectrum.

The glass P-50-Cu obtained by adding 1%  $CuO$  to P-50 glass was studied. The  $Cu^{2+}$  ions in P-50-Cu glass (Fig. 4) show a wide electronic absorption band in the region 700 – 900 nm and a transmission band from 490 to 550 nm. An absorption band peaking at 790 nm and a wide transmission band at 530 nm are observed in this glass. In addition, a weak inflection at 420 nm, whose origin is unclear, is seen in Fig. 4.

The EPR spectrum presented in Fig. 5 belongs to the  $Cu^{2+}$  ion. The electronic configuration  $3d^9$  of the outer shell with one electron needed to complete the  $d$  shell has the scheme of a split  $^2D$  state ground, antisymmetric ions with the configuration  $d^1$ , and a bottom doublet state  $^2E$ . This corresponds to a  $Cu^{2+}$  environment in the form of a tetragonally stretched oxygen octahedron (symmetry group  $D_{4h}$ ). The EPR spectrum is the same as the spectrum of  $V^{4+}$ , contains HFS lines due to the interaction of an unpaired electron of  $Cu^{2+}$  with the magnetic moments of the nuclei  $^{63,65}Cu$  ( $I = 3/2$ ). Four HFS lines corresponding to the orientation of the tetragonal axis parallel to the magnetic field are seen in the low-field part of the spectrum. In the perpendicular orientation, HFS is not resolved because of the small splitting of the HFS components. The parameters of the EPR spectrum are:  $g_{\parallel} = 2.416$ ,  $g_{\perp} = 2.062$ , and  $A_{\parallel} = 137 \times 10^{-4} \text{ cm}^{-1}$ .

Molybdenum in inorganic compounds exhibits valence state from II to VI. In glasses, Mo can be found in different states and gives color from blue and green-blue to yellow-brown. The oxidation state of Mo is difficult to identify from the optical spectra because of the existence of several valence forms of Mo and high sensitivity to the synthesis conditions. The  $Mo^{5+}$  ion is responsible for the EPR spectrum in glasses.

Glasses with the composition P-50 with 1%  $MoO_3$  (P-50-Mo) were synthesized.  $P_2O_5$  was introduced by three methods: 1) via phosphoric acid, 2) via ammonium phosphate, and 3) via ammonium phosphate +0.5% saccharin powder. It should be noted that when using method (2) the  $Mo^{5+}$  EPR signal is 30% stronger than that obtained with the first method and adding saccharin decreases this signal by 10%, apparently because of the reduction of  $Mo^{5+}$  to lower

oxidation states. The first method yields blue glass, the second green glass, and the third with brown glass. P-50-Mo glasses with different reducing agents (saccharin,  $\text{SnO}_2$ , their mixture,  $\text{NH}_4\text{Cl}$ , Si) were studied. With all these additives the glasses have a blue color of different intensity with the exception of 0.5% Si additive, for which the glass becomes dark gray.

Figure 6 shows that optical absorption spectrum of brown P-50-Mo glass (1). Strong absorption is seen in the short wavelength part of the spectrum, dropping linearly from 300 to 1000 nm, on which quite narrow bands at 380 and 460 nm and a weak inflection from 650 to 730 nm, rapidly decreasing in the direction of long wavelengths, are clearly manifested. In blue P-50-Mo glass (Fig. 6, spectrum 2), a single side band peaking at 720–730 nm is observed. The maximum of the transmission band lies at 480 nm.

In principle, the  $\text{Mo}^{5+}$  EPR spectrum has a complicated shape, due to the fact that Mo has several stable isotopes, of which two,  $^{95}\text{Mo}$  and  $^{97}\text{Mo}$ , have a magnetic moment (nuclear spin  $I = 5/2$ ); interaction of an unpaired electron of Mo results in the appearance of hyperfine structure (HFS). The content of magnetic isotopes is 25% of the total Mo content. For this reason, the spectra with the natural content of Mo isotopes do not show traces of HFS. The EPR spectrum is anisotropic with  $g_{\parallel} = 1.882$  and  $g_{\perp} = 1.933$ . The configuration of the outer electronic shell is  $d^1(4d^1)$ . The splitting of the five-fold degenerate orbital level is the same as in  $\text{Ti}^{3+}$  and  $\text{V}^{4+}$ . The values of the spectral parameters of  $\text{Mo}^{5+}$  EPR show that the ion is located in an environment with axial symmetry (group  $C_{4v}$ ) corresponding to a tetragonally compressed octahedron in which one bond ("molybdenyl") is much shorter than the others.

For P-50-Mo glass, the  $\text{Mo}^{5+}$  EPR signal is seen in blue and brown samples. The brown glass is obtained during melting under reducing conditions. Apparently, the lowest valence forms of molybdenum as well as colloidal particles of metallic Mo are present in it.

It follows from the data on the coloring of model aluminosilicate glasses by TE that elements such as Cu, V, Ti, and Mo can be found in states which in principle permit transmission in the blue and green parts of the optical spectrum and can be taken as the base for developing light filters with a prescribed transmission band. It should be noted that the introduction of Cr and W also makes it possible to obtain in these glasses transmission in the green-blue region of electromagnetic radiation. These ions are not considered here, since they have no advantages over the ones studied.

#### ALUMINUM SILICOPHOSPHATE GLASS CONTAINING TRANSITION-ELEMENT PAIRS

It is well known that a TE element present in melt can be in different states of oxidation depending on the time, the temperature and composition of the melt, and the atmosphere

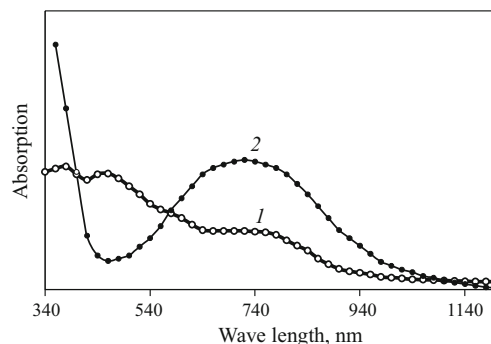


Fig. 6. Optical absorption spectrum of P-50-Mo glass: 1 and 2) brown and blue glass, respectively.

in the furnace. The oxidation state of the TE in commercial glasses is controlled not only by the gas atmosphere in the furnace and the synthesis temperature but also additions of oxidizing or reducing agents to the melt. There is no interaction between two TE in melt. Interaction occurs as the melt cools, when exchange with atmospheric oxygen slows down and the cooled melt can be regarded as a closed system. It is impossible to make a quantitative determination of the ratio of the oxidized and reduced forms of the oxides by means of chemical analysis; here, EPR is helpful, since in a number of cases the valence state of any particular TE can be determined only by means of EPR.

*Interaction of copper with different additives to aluminum silicophosphate glasses.* On the basis of the foregoing presentation, the  $\text{Cu}^{2+}$  ion possesses a wide transmission range in the green-blue part of the optical spectrum. For this reason, the effect of certain additives on the color characteristics of P-50 glass with 1%  $\text{CuO}$  added (P-50-Cu) was studied. No change of  $\text{Cu}^{2+}$  EPR signal strength is observed in P-50-Cu glass with 0.1%  $\text{V}_2\text{O}_5$  added. Here, the  $\text{V}^{4+}$  EPR signal is superposed on it and the transmission band shifts into the long-wavelength part — approximately to 540 nm — and the color becomes more saturated. These results show that for a weak interaction between Cu and V their optical spectra add.

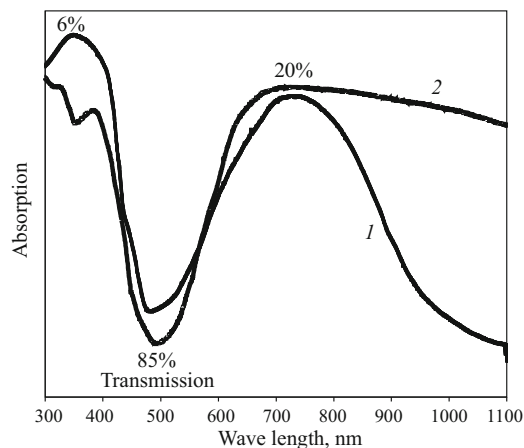
Some decrease of the coloring strength and weakening of the  $\text{Cu}^{2+}$  EPR signal by 30% is observed in P-50-Cu samples with 1%  $\text{TiO}_2$  added. This is probably due to the reaction  $\text{Ti}^{3+} + \text{Cu}^{2+} \rightarrow \text{Ti}^{4+} + \text{Cu}^{1+}$ . The transmission band shifts negligibly into the short-wavelength part of the spectrum.

When  $\text{CeO}_2$  is introduced the intensity of the  $\text{Cu}^{2+}$  EPR signal increases with  $\text{CeO}_2$  concentration as a result of the reaction  $\text{Cu}^{1+} + \text{Ce}^{4+} \rightarrow \text{Cu}^{2+} + \text{Ce}^{3+}$ .

In addition, the intensity of the coloring of the glass increases and the transmission band shifts weakly into the short-wavelength part of the spectrum, which could be due to the formation of Cu-O-Ce pairs.

*Interaction of copper and molybdenum.* When from 0.1 to 0.7%  $\text{CuO}$  is added to P-50 glass containing 1%  $\text{MoO}_3$  additivity of the  $\text{Cu}^{2+}$  and  $\text{Mo}^{5+}$  EPR spectra is observed, and as the  $\text{CuO}$  concentration increases, the  $\text{Cu}^{2+}$  EPR signal in-





**Fig. 7.** Optical absorption spectra of LB-16 glasses: 1) no CuO; 2) contains CuO.

tensity increases and that of  $\text{Mo}^{5+}$  decreases. It can be supposed that the reaction  $\text{Cu}^{1+} + \text{Mo}^{5+} \rightarrow \text{Mo}^{4+} + \text{Cu}^{2+}$  occurs between them. For about 0.5% CuO and addition of  $\text{CeO}_2$  a narrow transmission band peaking at about 500 nm can be obtained.

Glasses with composition close to the P-50 model, in which 3%  $\text{P}_2\text{O}_5$  was replaced by oxides of Zr, Cd, Ba, La, B, Ca, Mg, and other elements in order to improve the thermal and technological properties of the glass, were studied. A composition with nearly optimal properties was ultimately obtained (%): 55  $\text{P}_2\text{O}_5$ , 17.1  $\text{Al}_2\text{O}_3$ , 20  $\text{SiO}_2$ , 1.5  $\text{La}_2\text{O}_3$ , 2  $\text{ZrO}_2$ , 2.5  $\text{B}_2\text{O}_3$ , 1.5  $\text{MoO}_3$ , and 0.5 CuO (LB-15 glass).

Figure 7 displays the optical spectra of LB-16 glass without CuO (spectrum 1), which is the  $\text{Mo}^{5+}$  spectrum, and the spectrum of LB-16 glass containing Mo and Cu (spectrum 2).

Copper impurity improves the transmission band of the glass: it shifts the band in the required direction (500 nm) and equalizes the transmission in the red and IR regions due to the absorption bands from the forms of molybdenum with the lowest valence. The glass was obtained via ammonium molybdate with addition of 0.5% saccharin and 0.5%  $\text{SnO}_2$ .

## CONCLUSIONS

The EPR and optical spectra of different transition elements in  $\text{Al}_2\text{O}_3$ - $\text{P}_2\text{O}_5$ - $\text{SiO}_2$  glasses have been studied for this

first time. These glasses can serve as the base for obtaining green-blue light filters with sufficiently low CLTE  $(41 - 49) \times 10^{-7} \text{ K}^{-1}$  with heat-resistance 150°C in the annealed samples and 300°C in quenched samples.

It was shown that the most suitable colorants are copper oxide and molybdenum oxide. However, the color characteristics of each of them are highly sensitive to the reagents and the conditions of synthesis. Adding Cr and V as additives when using Cu and Mo as the main colorants changes the color of the glass because their spectra add. The required color characteristics can be obtained by adjusting the concentration of the impurities. The simultaneous presence of Mo and Cu in the glass makes it possible to obtain the required color characteristics by means of chemical reactions between these elements and with an appropriate choice of reagents and oxidizing-reducing agents. Glass with the composition (%) 55  $\text{P}_2\text{O}_5$ , 17.1  $\text{Al}_2\text{O}_3$ , 20  $\text{SiO}_2$ , 1.5  $\text{La}_2\text{O}_3$ , 2  $\text{ZrO}_2$ , 2.5  $\text{B}_2\text{O}_3$ , 1.5  $\text{MoO}_3$ , 0.5 CuO possesses a transmission band peaking at 500 nm; its technological attributes permit recommending such glasses for use as heat-resistant light filters.

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